The University of Chicago
Founded by John D. Rockefeller

The Addition Compounds of Organic Substances with Sulfuric Acid

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By CLIFFORD D. CARPENTER

1914

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THE ADDITION COMPOUNDS OF ORGANIC SUBSTANCES WITH SULFURIC ACID.

The treatment of aromatic organic substances with sulfuric acid, resulting in the formation of condensation products (sulfonic acids), is a well-known and widely-applied reaction. In a recent communication[1] the opinion was expressed that, in such condensations, the formation of addition compounds between the reacting substances may represent an intermediate stage of the process. The same view has been repeatedly advanced in the past, notably by Kekulé,[2] van't Hoff,[3] Michael,[4] and Guye.[5] Very little *systematic* evidence, however, has been brought forward in its support, save in the work of Menschutkin,[6] on the addition compounds of organic substances with inorganic salts, illustrating an intermediate phase of Friedel and Craft's reaction. The recent papers of Baume[7] and his pupils, on systems containing substances of very low freezing point, are also of importance.

Sulfonation is a vigorous reaction, induced by the application of heat. Of the mechanism of the process we know practically nothing, except that it is complex and probably consists of several distinct stages. Since, at the high temperatures employed, the reaction is rushed through all of these without a stop, no information has been obtained regarding possible intermediate products. Hoogewerff and van Dorp[8] have iso-

[1] Kendall, *J. Am. Chem. Soc.*, **36**, 1722 (1914).

[2] Kekulé, *Ann.*, **106**, 129 (1858).

[3] Van't Hoff, *Ansichten über organische Chemie*, I, 225, 244.

[4] Michael, *J. Am. Chem. Soc.*, **32**, 1001 (1910).

[5] Guye, *J. chim. phys.*, **8**, 119 (1910).

[6] Menschutkin, *J. chim. phys.*, **9**, 538 (1911).

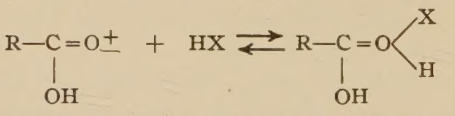
[7] Baume, *J. chim. phys.*, **12**, 212 (1914).

[8] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, **18**, 211 (1899); **21**, 353 (1902).

lated some addition compounds of organic substances with sulfuric and phosphoric acids, but a *complete* examination has been made of no single system.

In the present investigation, the freezing point method previously described[1] is applied to the general study of sulfonation. The components are mixed at as low a temperature as possible and the mixture *frozen* instead of *heated;* in this way addition compounds, if formed, are at once isolated. The freezing point (temperature of *incipient solidification*) of a mixture of known composition gives us a point on the temperature-composition curve of the system, and from a series of mixtures of varying composition the complete diagram is obtained. In this diagram a break in the curve corresponds to a change in the solid phase crystallizing from the solution; a maximum point on the curve indicates a compound. At such a maximum point the mixture completely solidifies at constant temperature. The position of the maximum on the axis of molecular composition gives the formula of the compound; the sharpness of the curve around the maximum shows the relative extent of dissociation of the compound into its components. Fuller details of the experimental method followed and of the interpretation of the diagrams obtained will be found on reference to the previous papers cited above.

The first class of substances examined consisted of the normal aromatic acids (benzoic acid and its homologs). It has already been shown[2] that these substances give addition compounds with stronger *organic* acids. In such systems the acidic properties of the weaker acid are suppressed and basic (unsaturated) properties are induced in the characteristic carbonyl group, the reaction taking place as follows:



The compounds formed are consequently to be regarded as true oxonium salts. It will be obvious that the same reaction should apply if the stronger acid of the system is *inorganic, e. g.*, sulfuric acid. The primary dissociation of this acid is monobasic, hence the compounds obtained should be of the general type indicated above, $R.COOH,H_2SO_4$. However, the secondary dissociation of sulfuric acid also involves the possibility of addition compounds of the type $2R.COOH,H_2SO_4$.

The experimental results obtained showed that the reaction proceeds exactly as expected, addition compounds of both types being isolated. The investigation was therefore extended to include other classes of organic substances containing the characteristic $>C=O^{\pm}$ group, namely

[1] Kendall, *J. Am. Chem. Soc.*, **36**, 1222 (1914).

[2] *Ibid.*, **36**, 1722 (1914).

aliphatic acids, aldehydes, ketones and anhydrides. All of these gave addition products with sulfuric acid. The action of sulfuric acid on phenols was also examined, with significant results. The complete list of substances studied is given below:

Aromatic acids.	Aliphatic acids.	Phenols.
1. Benzoic	10. Chloroacetic	15. Phenol
2. *o*-Toluic	11. Trichloroacetic	16. *o*-Cresol
3. *m*-Toluic	12. Crotonic	17. *p*-Cresol
4. *p*-Toluic	13. α-Chlorocrotonic	18. *p*-Xylenol
5. α-Toluic	14. Glutaric	19. *p*-Xylenol
6. Salicylic		20. Thymol
7. *o*-Nitrobenzoic		21. *o*-Nitrophenol
8. Cinnamic		22. *m*-Nitrophenol
9. Mandelic		23. *p*-Nitrophenol
Aldehydes.	**Ketones.**	**Anhydrides.**
24. *p*-Oxybenzaldehyde	28. Acetophenone	32. Benzoic
25. *p*-Nitrobenzaldehyde	29. Benzophenone	33. Succinic
26. Vanillin	30. Benzil	34. Phthalic
27. Piperonal	31. Dimethylpyrone	35. Coumarin

Experimental.

Pure sulfuric acid (100% H_2SO_4) was obtained by mixture of samples of higher and lower concentration, respectively. The acid of lower concentration employed was J. T. Baker's "Acid sulfuric, C. P. 95.6–96.4%," that of higher concentration was prepared from this by careful addition of Baker and Adamson's "Sulfuric acid, C. P. Fuming. ($H_2S_2O_7$)." The 100% acid thus obtained was standardized gravimetrically by the barium sulfate method. A more accurate criterion of its purity, however, was directly available in a determination of its freezing point, since a change in concentration of 0.1% corresponds to a difference of 0.6° in the point of fusion. The acid used throughout the investigation froze at 10.3–10.4°. This compares favorably with the values found by other observers,[1] when it is remembered that the acid could not be completely safeguarded from traces of moisture during the determinations. Contact with the outer air was made as short as possible by delivering the acid into the freezing point tube from a Grethan pipet.

The organic substances employed were mostly pure Kahlbaum specimens with satisfactory points of fusion. Only in a few cases was special purification necessary.

The experimental difficulties involved in the examination of the systems considered in the present paper were much greater than those encountered in previous work, and the method of procedure was necessarily

[1] Pickering, *J. Chem. Soc.*, **57**, 331 (1890) obtained 10.35° as the point of fusion. A slightly higher value—10.43° to 10.45°—was found by Lichty *J. Am. Chem. Soc.*, **30**, 1842 (1908)).

slightly modified to reduce them as much as possible. In the first place, all solutions with low temperatures of fusion became very viscous and hard to stir. What little stirring could be done produced in the liquid a mass of air bubbles, difficult to distinguish from minute crystals, hence the solution never became perfectly clear and the freezing point appeared very indeterminate. In such systems each point was repeated several times and after considerable practice the exact temperature of fusion could be fixed. Secondly, almost all mixtures exhibited supercooling to a marked degree. So long as the freezing point curve of one of the components was being followed, solidification could be induced by the addition of a minute crystal of this component, but nothing could be done in cases where, a compound being expected, the mixture persistently hardened to a glassy mass without crystallization. Finally, certain of the systems (especially phenols) gave dark-colored solutions, in which it was very difficult to determine the presence of solid phase, although a yellow flame set behind the tube proved of some help.

Pure sulfuric acid fumes on exposure to the air, even at ordinary temperatures, and tends to lose SO_3. This was not, however, a cause of difficulty in the systems considered in the present paper, since the addition of the second component, with the consequent formation of compounds in the solution, considerably reduces this tendency to decomposition. Even at temperatures above 100° (where little sulfuric acid was present) no indications of evolution of sulfur trioxide or water from the mixtures were obtained.

Sulfonation itself rarely took place at the temperature of experiment.[1] In cases where sulfonation did proceed rapidly, the fact could at once be recognized by the presence of condensed water on the exposed portion of the tube. Such systems were not examined further. It is quite certain that the compounds isolated by freezing, described in the following pages, are addition and not sulfonation products,[2] for the sulfonic acids decompose on fusion and have no definite freezing points. Also the maximum points on the curves always correspond to points of simple molecular composition, which would not be the case if the components had reacted together to split off water. Furthermore, the complete solidification of a solution at a maximum point at constant temperature indicates that no water is present.

It was found that the exact point of fusion of a mixture could be most readily determined as follows: Solidification was induced, and the whole

[1] Sulfonation is a slow process, even at high temperatures. Hence, at the freezing point of the mixture, its progress during the course of the experiments was generally negligible entirely. In a few systems, however, it was observed that the temperature of fusion of a mixture changed gradually with the time, pointing to slow sulfonation of the substance under investigation.

[2] This point is discussed more fully in a later section of the paper.

apparatus was placed in a water or paraffin bath, the temperature of which was slightly above the required freezing point, as found by a previous approximate determination. Stirring was constantly maintained in the solution, and the thermometer immersed in this indicated a gradual rise of temperature so long as solid phase was present and absorbing heat by fusion. Disappearance of solid phase was marked by a "hang" in the temperature, succeeded by a rapid rise. At the same time the solution became clear.

By this method freezing points could be obtained, in favorable cases, accurate to within 0.2–0.5°; in some systems, however, the temperatures given are correct only to the nearest degree. The difficulties of observation were especially great on the sulfuric acid side. Points in this region (solid phase H_2SO_4) are of no particular importance. Consequently, after the first series of experiments with the aromatic acids had been completed, the examination of this portion of the systems was omitted, except in special cases. The curve was started from the other end and carried along as far as possible, by successive additions of sulfuric acid, until the composition of the mixture was such that no further compounds were to be expected.

The results of the investigation are collected in the tables below, which are arranged as in the preceding papers of this series. (T = temperature of incipient solidification.) Some typical freezing point curves are shown in the accompanying diagrams.

Aromatic and Aliphatic Acids.

1. Benzoic Acid.—The compound $C_6H_5.COOH,H_2SO_4$ was obtained, stable at its maximum, m. p. 87.5°. The freezing point curve is given in Fig. I.

(*a*) Solid phase, $C_6H_5.COOH$.

% $C_6H_5.COOH$...	100.0	98.0	92.1	83.9	69.1	67.4
T.....	121.8	120.6	115.8	109.6	92.5	90.0

(*b*) Solid phase, $C_6H_5.COOH,H_2SO_4$.

% $C_6H_5.COOH$...	60.2	56.9	51.8	49.5	44.3	39.2	34.2	30.8
T.....	82.3	84.2	86.2	87.3	86.3	83.2	77.2	72.3
% $C_6H_5.COOH$...	26.2	24.2	22.6	18.6				
T.....	61.4	53.2	44.6	25.8				

(*c*) Solid phase, H_2SO_4.

% $C_6H_5.COOH$...	9.9	8.0	5.7	3.2	0.0
T.....	—6.2	—1.2	3.2	7.0	10.3

2. o-Toluic Acid.—The compound $C_7H_7.COOH,H_2SO_4$ was obtained, stable at its maximum, m. p. 59° (see Fig. III).

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	88.7	78.0	68.1	66.7	61.1	58.1
T.....	102.9	97.8	92.0	83.6	82.2	74.2	67.0

(*b*) Solid phase, $C_7H_7.COOH,H_2SO_4$.

% $C_7H_7.COOH$...	51.9	51.6	47.4	44.3	39.5	37.0	33.6
T.....	58.7	58.7	58.2	57.6	56.3	54.6	49.1
% $C_7H_7.COOH$...	30.7	25.6	20.1				
T.....	45.6	33.5	12.0				

(*c*) Solid phase, H_2SO_4.

% $C_7H_7.COOH$...	4.6	2.4	0.0
T.....	3.0	7.2	10.3

3. m-Toluic Acid.—In this system two compounds were isolated, $2C_7H_7.COOH,H_2SO_4$ (m. p. 79.5°, by extrapolation), and $C_7H_7.COOH,H_2SO_4$ (m. p. 63.5°, by extrapolation). Both compounds are unstable at their maxima, but their points of fusion may be readily obtained by a slight extension of the curves, as will be seen from the diagram (Fig. I).

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	84.5	74.3	67.7	64.1	61.8
T.....	110.0	100.5	92.0	83.6	78.7	74.9

(*b*) Solid phase, $2C_7H_7.COOH,H_2SO_4$.

% $C_7H_7.COOH$...	64.7	61.8	60.2	59.5	58.7	55.6	54.1	50.9
T.....	79.3	78.9	78.3	78.3	78.0	76.2	75.9	72.2
% $C_7H_7.COOH$...	49.9	47.1	45.0	36.3				
T.....	71.6	68.8	62.3	36.2				

(*c*) Solid phase, $C_7H_7.COOH,H_2SO_4$.

% $C_7H_7.COOH$...	42.5	39.7	36.4	34.8	34.0	30.8	27.1	22.4
T.....	61.8	58.4	55.6	54.0	52.7	46.5	37.5	20.8

(*d*) Solid phase, H_2SO_4.

% $C_7H_7.COOH$...	7.7	2.4	0.0
T.....	—1.8	7.3	10.3

4. p-Toluic Acid.—The compound $C_7H_7.COOH,H_2SO_4$ was obtained, unstable at its maximum (m. p. 100° by extrapolation). The freezing point curve is shown in Fig. I.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	84.2	71.0	62.9	59.6	55.2	51.3	49.6	46.8
T.....	180.2	167.5	154.7	143.7	137.5	127.0	116.0	111.2	100.2

(*b*) Solid phase, $C_7H_7.COOH,H_2SO_4$.

% $C_7H_7.COOH$...	45.5	42.2	37.1	32.8	28.1	23.0	21.2	16.8	14.7
T.....	99.5	98.9	94.9	88.5	77.5	58.7	53.0	18.0	7.5

(*c*) Solid phase, H_2SO_4.

% $C_7H_7.COOH$...	6.2	3.2	1.7	0.0
T.....	—2.2	3.0	5.8	10.3

5. α-Toluic Acid.—The compound $C_7H_7.COOH,H_2SO_4$ was obtained, stable at its maximum, m. p. 62°.

(*a*) Solid phase, $C_7H_7.COOH$.

% $C_7H_7.COOH$...	100.0	91.1	83.8	71.6	69.9	68.7	67.1	65.3	61.6
T.....	76.8	71.5	67.7	59.4	56.8	55.0	53.2	50.1	40.6

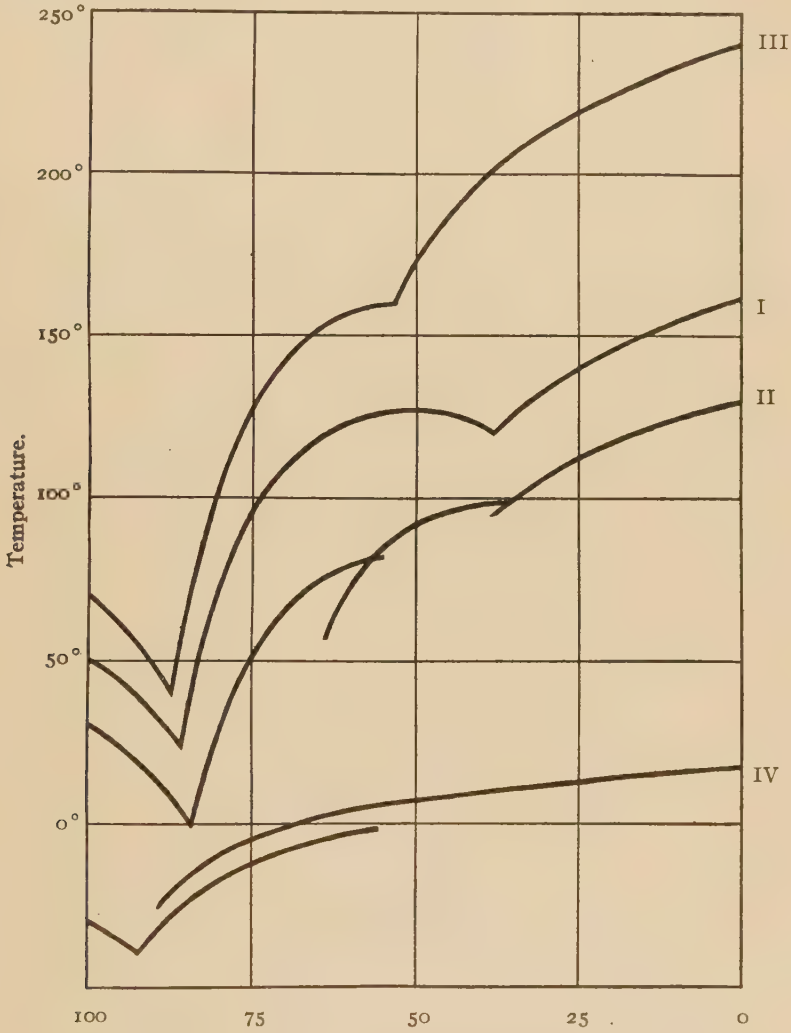
(*b*) Solid phase, $C_7H_7.COOH,H_2SO_4$.

% $C_7H_7.COOH$...	56.3	53.7	49.8	45.1	42.6	39.5	37.9	36.2	28.7	16.3
T.....	58.4	60.0	61.7	61.2	60.7	60.0	58.7	55.0	47.7	15.8

(*c*) Solid phase, H_2SO_4.

% $C_7H_7.COOH$...	6.8	5.1	2.5	0.0
T.....	—9.0	—3.0	5.6	10.3

6. Salicylic Acid.—When sulfuric acid was added to this substance and the temperature raised to melt the solid, water was given off. This evidence of a condensation reaction rendered further work on the system useless.



I. Benzoic acid. Subtract 40° from temperature scale.
II. *m*-Toluic acid. Subtract 20° from temperature scale.
III. *p*-Toluic acid. Subtract 60° from temperature scale.
IV. Trichloroacetic acid. Add 40° to temperature scale.

Fig. I.

7. o-Nitrobenzoic Acid.—On an attempt to melt the mixture of acids in this case, a violent reaction took place, leaving nothing in the tube but a charred mass.

8. Cinnamic Acid.—This acid also charred with sulfuric acid when the temperature was raised, and no investigation of the system could be made. Hoogewerff and van Dorp[1] record the existence of two addition compounds with the formulas $C_8H_7.COOH,H_2SO_4$ and $2C_8H_7.COOH,3H_2SO_4$, respectively.

9. Mandelic Acid.—Here again the mixture of the two acids darkened on heating and no satisfactory examination of the system could be carried out.

10. Chloroacetic Acid.—No compound formation in this system was indicated.

(*a*) Solid phase, $CH_2Cl.COOH$.

% $CH_2Cl.COOH$.	100.0	94.4	88.1	78.9	65.1	62.3	59.7	53.7	46.0
T.....	61.7	60.5	57.8	52.7	41.1	38.1	34.5	25.2	9.2

11. Trichloroacetic Acid.—The freezing point curve of this system is given in Fig. I. It will be seen that the depression of the freezing point of trichloroacetic acid by sulfuric acid is abnormally small. No compound was isolated, but in the region between 11% and 44% trichloroacetic acid the points obtained fall on two regular curves running parallel throughout. It is evident that the lower curve corresponds to an unstable crystalline modification of trichloroacetic acid, with a melting point of approximately 50°.

(*a*) Solid phase, $CCl_3.COOH$ (I).

% $CCl_3.COOH$...	100.0	89.3	78.1	68.2	58.3	54.0	49.5	41.7	37.7
T.....	57.3	56.1	53.4	51.2	49.2	47.9	47.0	44.8	42.6
% $CCl_3.COOH$...	33.2	30.8	26.1	24.9	21.0	17.9	14.1	11.3	
T.....	41.9	39.2	39.5	35.3	31.7	29.0	21.6	15.5	

(*a*) Solid phase, $CCl_3.COOH$ (II).

% $CCl_3.COOH$...	43.9	32.9	21.9	17.8	13.4	7.8
T.....	38.4	33.8	24.0	20.2	13.4	1.0

(*b*) Solid phase, H_2SO_4.

% $CCl_3.COOH$...	2.9	0.0
T.....	7.5	10.3

12. Crotonic Acid.—This acid gave with sulfuric acid the equimolecular addition compound $C_3H_5.COOH,H_2SO_4$, stable at its maximum, m. p. 24.5°.

(*a*) Solid phase, $C_3H_5.COOH$.

% $C_3H_5.COOH$...	100.0	93.8	83.5	74.6	69.1	65.9	59.3
T.....	71.0	67.5	61.9	54.7	47.0	40.4	22.3

(*b*) Solid phase, $C_3H_5.COOH,H_2SO_4$.

% $C_3H_5.COOH$...	54.9	49.7	43.5	38.1	33.7
T.....	21.3	24.3	23.3	15.8	1.5

13. α-Chlorocrotonic Acid.—Here no addition compounds are indicated by the freezing point curve.

(*a*) Solid phase, $C_3H_4Cl.COOH$.

% $C_3H_4Cl.COOH$.	100.0	90.4	80.2	69.4	63.5	56.6	52.8
T.....	99.0	93.5	86.5	79.5	73.2	64.0	58.5
% $C_3H_4Cl.COOH$.	48.1	43.9	39.0	31.0			
T.....	49.5	41.0	30.0	2.0			

14. Glutaric Acid.—Hoogewerff and van Dorp[2] isolated addition compounds of

[1] Hoogewerff and van Dorp, *Rev. trav. chim. Pays-Bas*, 18, 213 (1899).

[2] *Loc. cit.*

sulfuric acid with the following dibasic aliphatic acids: succinic, fumaric, mesaconic. These proved unsuitable for use in the present investigation owing to their high points of fusion, and glutaric acid, which possesses the lowest melting point of the series of saturated dibasic acids, was chosen for examination. An equimolecular addition compound was obtained, stable at its maximum, m. p. 45.5°.

(*a*) Solid phase, $C_3H_6(COOH)_2$.

% $C_3H_6(COOH)_2$.	100.0	87.4	78.8	70.9	65.2	59.6	54.1	49.0	47.8
T.....	95.8	92.9	88.6	82.5	75.7	63.9	51.7	37.1	35.0

(*b*) Solid phase, $C_3H_6(COOH)_2,H_2SO_4$.

% $C_3H_6(COOH)_2$.	45.5	41.6	39.0	33.5
T.....	49.7	47.7	46.0	40.1

Consideration of Results with Acids.

Fourteen acids have been investigated with sulfuric acid. Four of these suffered decomposition on heating, three gave no addition compounds, and seven yielded positive results. Of the eight compounds isolated, seven were of the type $R.COOH,H_2SO_4$, and one of the type $2R.COOH,H_2SO_4$. All compounds were colorless.

An examination of the results shows that the rule enunciated in a previous communication,[1] that the tendency towards addition-compound formation (for acids in pairs) is dependent upon the difference in acidic strengths, holds throughout the entire series. Very weak organic acids readily form addition compounds with a strong acid, such as sulfuric acid. An increase in the acidic strengths of the organic acid is accompanied by the loss of this property. This is illustrated in the following table where the results of the present investigation and those obtained by Hoogewerff and van Dorp[2] are collected. The dissociation constants are those given by Ostwald.[3]

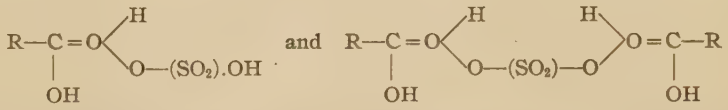
Acids forming addition compounds.		Acids not forming addition compounds.	
Acid.	100 *K*.	Acid.	100 *K*.
Benzoic.....	0.0060	*o*-Chlorobenzoic.....	0.132
o-Toluic.....	0.0120	*m*-Chlorobenzoic(?).....	0.0155
m-Toluic (2 compounds).....	0.00514	*p*-Chlorobenzoic(?).....	0.0093
p-Toluic.....	0.00515	*o*-Bromobenzoic.....	0.145
α-Toluic.....	0.00556		
m-Bromobenzoic.....	0.0137		
Cinnamic (2 compounds).....	0.00355		
Crotonic.....	0.00204	Chloroacetic.....	0.155
Succinic.....	0.00665	Trichloroacetic.....	121.0
Glutaric.....	0.00475	α-Chlorocrotonic.....	0.072
Fumaric.....	0.093		
Mesaconic.....	0.0790		

[1] Kendall, *Loc. cit.*

[2] Hoogewerff and van Dorp, *Loc. cit.* It must be remembered that negative results obtained by Hoogewerff and van Dorp do not disprove the existence of addition products, since the mixtures investigated by them may not have had compositions suitable for the isolation of compounds.

[3] Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

The results of the above table agree with those obtained previously[1] in indicating that addition compounds of the type acid–acid are, in fact, *oxonium salts*, the acidic properties of the weaker acid being suppressed by the stronger, and basic (unsaturated) properties being induced in the carbonyl group. Under this view the formulas of the compounds obtained are:



In the former, sulfuric acid acts as a monobasic acid; in the latter, as a dibasic acid.

Phenols.

15. Phenol.—The compound $2C_6H_5OH,H_2SO_4$ was obtained, stable at its maximum, m. p. 15.5° (see Fig. III).

(*a*) Solid phase, $C_6H_5.OH$.

% $C_6H_5.OH$.....	100.0	94.1	86.6	79.4	72.0
T.....	42.4	35.5	30.5	23.4	13.4

(*b*) Solid phase, $2C_6H_5.OH,H_2SO_4$.

% $C_6H_5.OH$.....	66.8	61.3	55.4	51.8	49.5	45.7	42.7	39.5
T.....	15.0	16.0	12.2	10.4	8.0	6.0	2.5	—2.0
% $C_6H_5.OH$.....	36.3	34.1						
T.....	—7.0	—10.0						

16. o-Cresol.—In this system no addition compounds could be isolated, supercooling making a satisfactory investigation very difficult.

(*a*) Solid phase, $C_7H_7.OH$.

% $C_7H_7.OH$.....	100.0	89.1	76.8	68.7	66.2	61.9
T.....	30.4	26.2	18.8	9.6	6.2	1.0

17. p-Cresol.—Here two compounds were isolated, both stable at their points of fusion; $2C_7H_7OH,H_2SO_4$ (m. p. 11.0°) and $C_7H_7.OH,2H_2SO_4$ (m. p. 93.5°). The flatness of the maximum in the case of the former compound indicates that it is largely dissociated into its components on fusion, but the form of the curve for the second addition product, together with its surprisingly high melting point, makes it evident that the compound is very stable. The freezing point curve is given in Fig. II.

(*a*) Solid phase, $C_7H_7.OH$.

% $C_7H_7.OH$.....	100.0	90.4	82.2	75.4	
T.....	34.6	29.4	22.1	11.6	

(*b*) Solid phase, $2C_7H_7.OH,H_2SO_4$.

% $C_7H_7.OH$.....	68.0	62.6	58.5	54.1	50.5	45.4
T.....	11.0	11.0	9.3	7.5	5.0	9.0

(*c*) Solid phase, $C_7H_7.OH,2H_2SO_4$.

% $C_7H_7.OH$.....	56.0	48.7	39.5	34.7	33.8	28.6	21.6	16.2	12.5
T.....	24.0	57.3	84.1	91.9	93.4	90.9	78.2	57.8	40.2

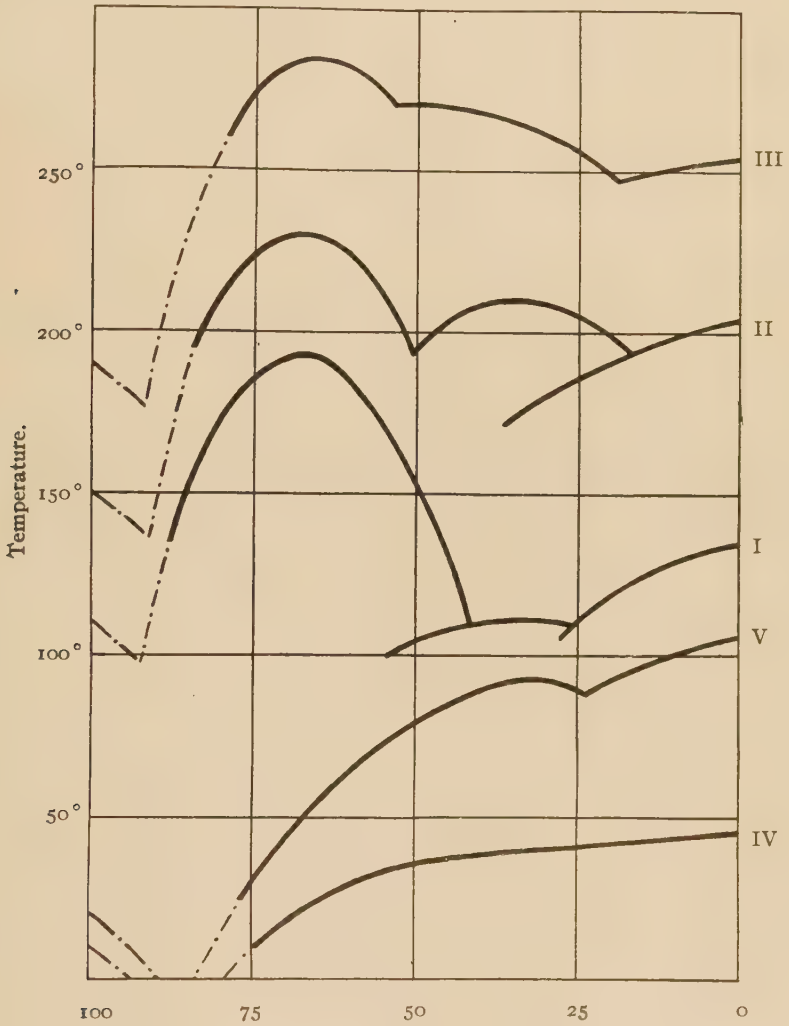
18. o-Xylenol.—In this system two compounds were also isolated, analogous to those obtained in the case of *p*-cresol. The compounds $2C_8H_9OH,H_2SO_4$ (m. p. 70°)

[1] Kendall, *J. Am. Chem. Soc.*, 36, 1722 (1914).

and $C_8H_9.OH,H_2SO_4$ (m. p. 90°) were obtained. Both are stable at their melting points (see Fig. II).

(*a*) Solid phase, $C_8H_9.OH$.

% $C_8H_9.OH$.....	100.0	87.5	80.2	75.8	72.1	63.7
T.....	63.7	57.6	50.3	47.0	42.4	31.6



I. *p*-Cresol. Subtract 100° from temperature scale.
II. *o*-Xylenol. Subtract 140° from temperature scale.
III. *p*-Xylenol. Subtract 180° from temperature scale.
IV. *o*-Nitrophenol. Temperature scale correct.
V. *m*-Nitrophenol. Subtract 10° from temperature scale.

Fig. II.

(*b*) Solid phase, $2C_8H_9.OH,H_2SO_4$.

% $C_8H_9.OH$.....	70.9	66.9	60.2	54.4
T.....	68.0	70.0	68.9	63.4

(*c*) Solid phase, $C_8H_9.OH,H_2SO_4$.

% $C_8H_9.OH$.....	50.7	47.8	44.6	41.5	34.0	30.4	25.3	20.3	16.1
T.....	53.8	60.8	71.5	80.7	90.0	89.4	84.8	72.8	58.3

19. p-Xylenol.—Two addition compounds were obtained in this system, the equimolecular compound $C_8H_9.OH,H_2SO_4$ (m. p. 91°) and the compound $C_8H_9.OH,2H_2SO_4$ (m. p. 104°). Both are stable at their maxima (see Fig. II).

(*a*) Solid phase, $C_8H_9.OH$.

% $C_8H_9.OH$	100.0	91.1	81.1
T.....	74.0	71.0	67.9

(*b*) Solid phase, $C_8H_9.OH,H_2SO_4$.

% $C_8H_9.OH$.....	71.7	67.0	61.7	54.0
T.....	80.6	84.2	87.2	90.4

(*c*) Solid phase, $C_8H_9.OH,2H_2SO_4$.

% $C_8H_9.OH$.....	46.4	40.1	32.8	24.7
T.....	92.4	101.0	104.0	91.9

20. Thymol.—On first addition of sulfuric acid to thymol the point of fusion was lowered, as in normal cases. After about 20% of acid had been added, however, two immiscible layers formed, and the point of fusion (in the layer richer in thymol) remained practically constant on further addition of acid. An attempt to cause complete admixture of the two liquids (at the point 53% thymol) by raising the temperature resulted in sulfonation taking place, a white solid separating out. This did not melt at 100°, at which temperature water was given off. The system was not examined further.

(*a*) Solid phase, $C_{10}H_{13}.OH$.

% $C_{10}H_{13}.OH$.....	100.0	92.4	83.3	72.2	64.7	52.7
T.....	49.6	47.1	43.0±	42.0±	42.0±	?

21. o-Nitrophenol.—No addition compound was here isolated. The form of the curve indicates also that none is present in solution, the freezing point depression being extremely small (see Fig. II). *o*-Nitrophenol here behaves quite differently from its isomers, *m*-nitrophenol and *p*-nitrophenol. Both of these form addition compounds, as will be seen in Tables XXII and XXIII below. Similarly *o*-nitrophenol does not yield addition products with aniline[1] or with dimethylpyrone,[2] while the other nitrophenols give compounds in both cases. This anomalous behavior of *o*-nitrophenol is evidently connected in some way with stearic hindrance, since in acidic strength it lies between the other two[3] and should give exactly similar results.

(*a*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_6H_4.NO_2.OH$.	100.0	93.6	88.0	82.3	75.7	74.4	68.9	67.9
T.....	45.0	43.9	42.4	41.5	40.7	41.4	39.5	40.6
% $C_6H_4.NO_2.OH$.	66.5	63.8	59.3	52.6	45.6	40.7	32.0	25.8
T.....	39.1	38.7	39.3	37.0	33.5	30.0	21.0	11.0

[1] Kreeman and Rodinis, *Monats.*, **27**, 136 (1906).

[2] Kendall, *J. Am. Chem. Soc.*, **36**, 1237 (1914).

[3] Holleman, *Rec. trav. chim. Pays-Bas*, **21**, 444 (1902).

22. m-Nitrophenol.—One compound was obtained, $2C_6H_4.NO_2.OH,H_2SO_4$, (m. p. 83°), stable at its maximum (see Fig. 2).

(*a*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_6H_4.NO_2.OH$.	100.0	93.3	87.7	82.0
T.....	95.4	92.5	89.4	84.7

(*b*) Solid phase, $2C_6H_4.NO_2.OH,H_2SO_4$.

% $C_6H_4.NO_2.OH$.	73.5	68.5	60.5	55.2	51.4	45.9	37.7	31.7	24.7
T.....	81.7	82.7	78.6	73.5	69.4	62.3	52.2	39.4	18.0

23. p-Nitrophenol.—Here also one compound was obtained, $2C_6H_4.NO_2,H_2SO_4$, (m. p. 90°), stable at its maximum.

(*a*) Solid phase, $C_6H_4.NO_2.OH$.

% $C_6H_4.NO_2.OH$.	100.0	92.7	83.9	76.9
T.....	113.8	109.4	102.7	97.0

(*b*) Solid phase, $2C_6H_4.NO_2.OH,H_2SO_4$.

% $C_6H_4.NO_2.OH$.	68.1	64.1	58.4	53.0	50.6	44.7	35.6
T.....	89.9	88.3	80.7	73.5	70.4	60.3	35.1

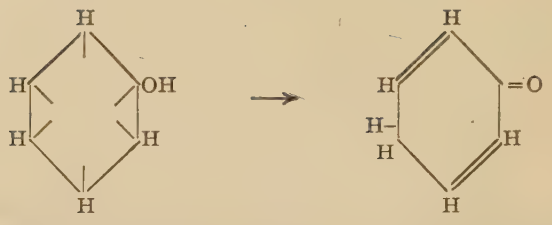
Consideration of the Results with Phenols.

Nine phenols have been investigated with sulfuric acid. One of them suffered sulfonation, two gave negative results, the remaining six yielded addition compounds. Of the nine compounds isolated, five were of the type $2R.OH,H_2SO_4$, one of the type $R.OH,H_2SO_4$, and three of the type $R.OH,2H_2SO_4$.

The addition of sulfuric acid to a phenol is accompanied in general by a darkening in color, the mixture becoming red and in some cases almost black. Only in one system, *p*-cresol, were the solutions light-colored throughout. In the solid form, however, the addition products were colorless, or at most, only faintly tinted. This darkening, coupled with the viscous nature of the mixture, made the investigation of the systems extremely difficult. Supercooling occurred, in almost all systems, to a considerable extent; so that in some cases a compound (*e. g.*, the compound $2C_8H_9.OH,H_2SO_4$, in the case of *p*-xylenol) was entirely missed on the first examination, and only on a repetition of the experiment found to exist. It is extremely probable, consequently, that in certain systems some of the addition products present in solution were not isolated.

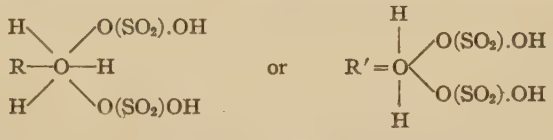
With regard to the structural formula of the compounds obtained, it is rather difficult to decide. The analogy between the addition products here described and those obtained in the case of organic acids renders the same oxonium structure extremely probable. The generally accepted view[1] for the representation of compounds of the type phenol-acid assumes that the phenol first goes over to the tautomeric ketonic form, *e. g.*,

[1] Gomberg and Cone, *Ann.*, **376**, 220 (1910).



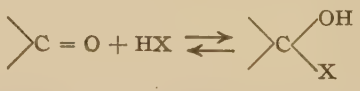
On this assumption, addition takes place on the carbonyl group, as in the case of acids. But it is also possible for the reaction to be explained directly, by assuming addition on the —OH group, as in the case of alcohols.[1]

According to either of the above hypotheses, it is easy to represent compounds of the types $R.OH,H_2SO_4$ and $2R.OH,H_2SO_4$. In the former sulfuric acid acts as a monobasic acid, in the latter as a dibasic acid. The third type of compound, however, $R.OH,2H_2SO_4$, presents some difficulties, since it is impossible to express it, under the scheme followed throughout this series of papers, except by the assumption of hexavalent oxygen.



This assumption has previously been made by McIntosh[2] to explain the compounds obtained with dimethylpyrone and the halogen acids. It is, of course, supported by the hexavalency of sulfur.

While the structural formula of the compounds phenol-acid cannot be definitely fixed, it may be pointed out here that it is impossible to represent compounds of the third type under the hypothesis that these products are carbonium salts.[3] According to this theory an equimolecular addition compound is considered to be formed as follows:



addition taking place through the breaking up of the double bond of the carbonyl linkage. It is obvious, however, that a compound of the formula $R.OH,2H_2SO_4$ cannot be represented according to this view, and an oxonium structure must be admitted.

The investigation of systems of the type phenol-acid is at present being continued.

Aldehydes, Ketones and Anhydrides.

24. p-Oxybenzaldehyde.—On addition of sulfuric acid to this substance, a dark red

[1] Maass and McIntosh, *J. Am. Chem. Soc.*, **30**, 1284 (1912).

[2] McIntosh, *Ibid.*, **32**, 542 (1910).

[3] Gomberg and Cone, *Ann.*, **376**, 220 (1910).

coloration was produced. When the temperature was raised, charring occurred, and the investigation of the system could not be continued.

25. p-Nitrobenzaldehyde.—No addition compound was isolated.

(*a*) Solid phase, $C_6H_4.NO_2.CHO$.

% $C_6H_4.NO_2.CHO$	100.0	90.6	79.7	73.2	65.0	55.4	49.7	49.5
T	104.4	100.7	94.8	90.9	85.0	76.6	74.5	74.8
% $C_6H_4.NO_2.CHO$	47.3	44.6	43.9	41.1	40.2	34.5	33.7	24.1
T	73.0	70.4	70.4	67.1	66.7	54.0	56.5	32.6

26. Vanillin.—When sulfuric acid was added, the mixture became dark-colored and decomposition began to occur, so that no examination of the system could be made. Hoogewerff and van Dorp[1] record the isolation of an equimolecular compound.

27. Piperonal.—Here again darkening of the mixture prevented any examination of the system. Hoogewerff and van Dorp, however, record having isolated the following compound: $2C_6H_3(O_2CH_2).COH,3H_2SO_4$.

28. Acetophenone.—The compound $2CH_3.CO.C_6H_5,H_2SO_4$ was obtained, stable at its maximum (m. p. 29°). The system could not be completely investigated owing to the fact that the solutions became dark and viscous.

(*a*) Solid phase, $CH_3.CO.C_6H_5$.

% $CH_3.CO.C_6H_5$	100.0	95.8	95.2	89.0
T	18.7	17.2	17.4	13.9

(*b*) Solid phase, $2CH_3.CO.C_6H_5,H_2SO_4$.

% $CH_3.CO.C_6H_5$	86.3	80.8	69.0	68.9	68.6	63.0	59.9	54.9	51.1
T	17.6	23.8	28.4	28.7	29.9	28.0	25.0	22.5	18.5

29. Benzophenone.—The compound $C_6H_5.CO.C_6H_5,H_2SO_4$ was obtained, stable at its maximum (m. p. 64° (see Fig. III)).

(*a*) Solid phase, $C_6H_5.CO.C_6H_5$.

% $C_6H_5.CO.C_6H_5$	100.0	96.4	92.9	88.7	79.8	70.9
T	47.8	46.4	44.5	42.1	38.0	26.5

(*b*) Solid phase, $C_6H_5.CO.C_6H_5,H_2SO_4$.

% $C_6H_5.CO.C_6H_5$	64.5	54.1	46.2	42.6	38.8	35.7	32.6	29.6
T	56.6	63.0	63.9	61.9	59.4	55.2	48.7	39.1

30. Benzil.—Darkening of the mixture here made an examination impossible. Hoogewerff and van Dorp record the isolation of an equimolecular compound.

31. Dimethylpyrone.—Three compounds of this substance with sulfuric acid were isolated: $2C_7H_8O_2,H_2SO_4$ (m. p. 103.6°), $C_7H_8O_2,H_2SO_4$ (m. p. 96°), and $2C_7H_8O_2,3H_2SO_4$ (m. p. 44.8). The first and third of these are just stable at their maxima. Mixtures containing less than 30% dimethylpyrone supercooled to a solid glassy mass, consequently the system could not be completed. It seems probable from the form of the curve (see Fig. III) that other compounds exist. Dimethylpyrone is a stronger base than any of the other substances investigated in this paper; the addition compounds formed, therefore, are very little dissociated on fusion. The curve recalls strongly that of the system sulfuric acid–water, the latter substance being of approximately the same basic strength as dimethylpyrone.[2]

(*a*) Solid phase, $C_9H_8O_2$

% $C_9H_8O_2$	100.0	85.4	76.1	71.5
T	132.0	124.0	115.0	109.0

[1] Hoogewerff and van Dorp, *Loc. cit.*

[2] Walker, *Ber.*, **34**, 4115 (1901).

(*b*) Solid phase, $2C_9H_8O_2,H_2SO_4$.

% $C_9H_8O_2$.....	66.9	63.5	61.1	57.3	55.5
T.....	103.6	101.8	100.2	90.4	84.2

(*c*) Solid phase, $C_9H_8O_2,H_2SO_4$.

% $C_9H_8O_2$.....	53.0	51.3	50.6	47.1	46.2	43.3	41.8	40.5	40.1
T.....	88.1	93.4	96.0	93.4	90.9	72.5	56.0	41.6	36.6

(*d*) Solid phase, $2C_9H_8O_2,3H_2SO_4$.

% $C_9H_8O_2$.....	39.5	38.3	36.1	34.1	32.2	30.4
T.....	44.3	43.1	37.6	29.3	18.2	6.0

32. Benzoic Anhydride.—In this system three compounds were obtained: $2C_{14}H_{10}O_3,H_2SO_4$ (m. p. 52.5°, by extrapolation), $C_{14}H_{10}O_3,H_2SO_4$ (m. p. 70.5°) and $C_{14}H_{10}O_3,2H_2SO_4$ (m. p. 60°). The first of these is unstable at its maximum point, the others are stable. The freezing point curve is given in Fig. III.

(*a*) Solid phase, $C_{14}H_{10}O_3$.

% $C_{14}H_{10}O_3$.....	100.0	94.8
T.....	39.5	38.9

(*b*) Solid phase, $2C_{14}H_{10}O_3,H_2SO_4$.

% $C_{14}H_{10}O_3$.....	90.2	85.7	81.0	77.2	73.5
T.....	42.3	45.3	49.2	50.0	51.0

(*c*) Solid phase, $C_{14}H_{10}O_3,H_2SO_4$.

% $C_{14}H_{10}O_3$.....	67.6	62.2	55.4	49.7	43.7	37.8	37.4
T.....	57.3	64.3	69.4	70.2	67.6	59.1	58.3

(*d*) Solid phase, $C_{14}H_{10}O_3,2H_2SO_4$.

% $C_{14}H_{10}O_3$.....	36.1	31.5	26.5	15.8
T.....	58.7	58.7	55.4	25.0

33. Succinic Anhydride.—The study of this system proved unsatisfactory, as the anhydride sublimes extremely readily at high temperatures. No conclusive results were obtained.

34. Phthalic Anhydride.—This system also gave no definite results.

35. Coumarin.—The compound $C_9H_6O_2,H_2SO_4$ was obtained, stable at its maximum, (m. p. 35.5°).

(*a*) Solid phase, $C_9H_6O_2$.

% $C_9H_6O_2$.....	100.0	89.2	80.7	73.1	68.3	63.5	58.4
T.....	68.4	62.3	53.4	51.8	46.5	40.4	30.8

(*b*) Solid phase, $C_9H_6O_2,H_2SO_4$.

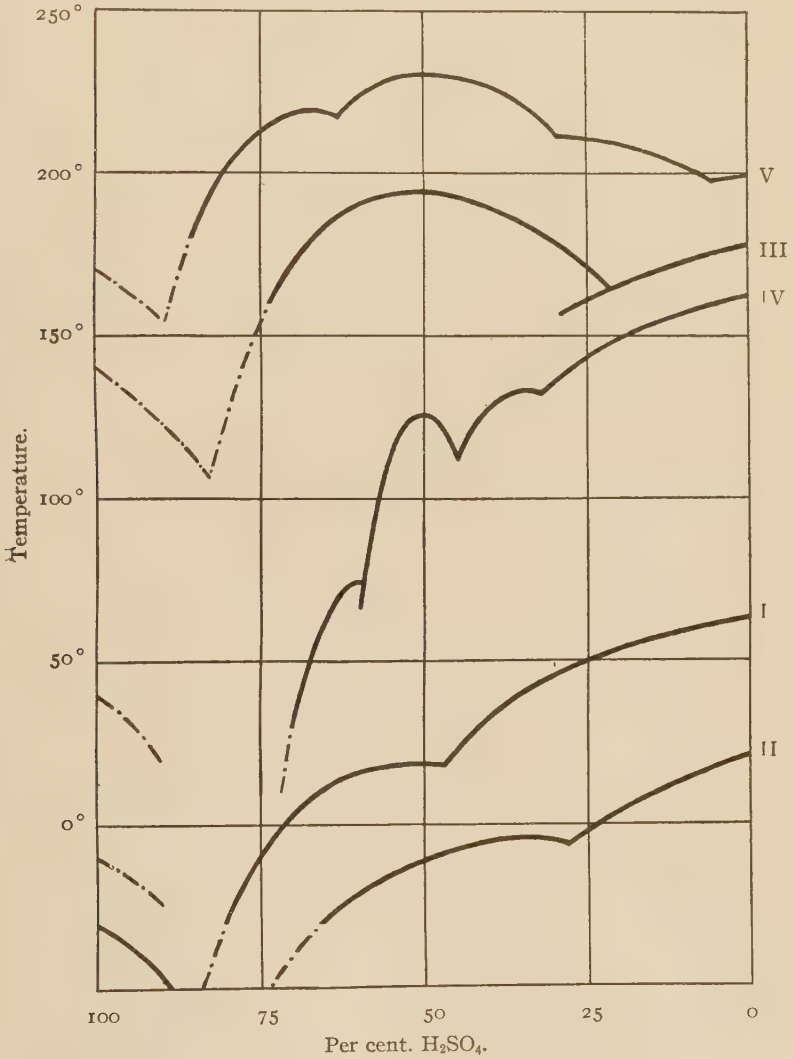
% $C_9H_6O_2$.....	54.2	50.5	46.2	42.6	38.4	35.2
T.....	32.7	35.5	34.5	32.3	24.0	14.0

Consideration of Results with Aldehydes, Ketones and Anhydrides.

From the twelve systems investigated, nine addition compounds were isolated. The four aldehydes examined gave no definite results, yet it must not be assumed from this that aldehydes do not react with sulfuric acid to form addition compounds, for with diluted acid Hoogewerff and van Dorp obtained compounds in the cases of piperonal and vanillin. The fact is that, in most cases, the reaction is so violent that the process is carried past the addition stage. Aldehydes, in general, exhibit a greater

tendency than ketones to form addition products with acids, as will be shown in a subsequent paper dealing more fully with these two classes of substances.

The four ketones here investigated gave five addition products. Aceto-



I. *o*-Toluic acid. Add 40° to temperature scale.
II. Phenol. Add 20° to temperature scale.
III. Benzophenone. Subtract 130° from temperature scale.
IV. Dimethylpyrone. Subtract 30° from temperature scale.
V. Benzoic anhydride. Subtract 160° from temperature scale.

Fig. III.

phenone and benzophenone yielded compounds of the types $2R,CO.R',H_2SO_4$ and $R,CO.R,H_2SO_4$, respectively. In the former, sulfuric acid acts as a dibasic acid, in the latter as a monobasic acid. Dimethylpyrone gave compounds of both these types, and also the addition product $2C_7H_8O_2,3H_2SO_4$. Compounds of this type have previously been obtained with dimethylpyrone and other acids.[1]

The four anhydrides investigated gave four addition products. Two of these were equimolecular, the others were of the formulas $2C_{14}H_{10}O_3$, H_2SO_4 and $C_{14}H_{10}O_3,2H_2SO_4$, respectively. In a substance such as benzoic anhydride the possibilities for addition compound formation are so numerous that no structural representation of the products isolated is attempted.

General Conclusions.

Thirty-five organic substances in all have been investigated with sulfuric acid, and twenty-six addition compounds have been obtained. These include:

9 compounds of the type A_2B (A = organic substance, B = sulfuric acid).

12 compounds of the type AB (or A_2B_2).

1 compound of the type A_2B_3.

4 compounds of the type AB_2 (or A_2B_4).

It is thus seen that the compounds form a regular series in four steps. These compounds have been explained on the assumption of oxonium salt formation developed in previous papers.[2] The quantitative results, where available, are in complete accordance with this view.

The reasons for asserting definitely that these compounds are addition and not sulfonation products—a point already briefly referred to in the introduction—may here be discussed more fully. The freezing point curves shown above offer in themselves sufficient evidence in proof of this important point, since all maxima appear at points of simple molecular composition. This could occur only by chance if the reaction in-

[1] Kendall, *Loc. cit.*

[2] Kendall, *Loc. cit.* The substances examined all contain oxygen; in cases where this element is absent (*e. g.*, aromatic hydrocarbons) a new explanation must be sought. In the first place, the addition might take place by means of the unsatisfied carbon valences of the benzene ring. This is supported by the fact that the saturated aliphatic hydrocarbons do not form sulfonation products. On the other hand, no evidence has been obtained throughout the present series of investigations of any difference in behavior between aliphatic and aromatic substances which would indicate activity of such a nature. An alternative hypothesis (first suggested to us by Dr. J. M. Nelson) is that the carbon atom is potentially hexavalent, just as the oxygen atom is potentially quadrivalent. The addition process would thus be essentially similar in its nature to that investigated in this paper, the basic properties of carbon, however, probably being found much weaker than those of oxygen. It is hoped to investigate this point after the study of the different classes of oxonium compounds has been completed.

volved were sulfonation and not addition, and that such a chance could happen twenty-six times without a single exception is a manifest impossibility. Furthermore, sulfonation takes place with splitting-off of water, and in no case (except those expressly mentioned above) was evolution of water observed. The fact that complete solidification at constant temperature occurs at a maximum point is decisive proof that a pure substance is under examination and it is very improbable[1] that this pure substance can be other than an addition product.

Another fact is extremely important in this connection. Sulfonation is, even at high temperatures, a slow reaction, while all products isolated in this paper are formed immediately. For instance, a basic substance such as aniline must be heated with sulfuric acid to 180–190° for *four or five hours* before sulfonation is complete.[2] On the other hand, when *p*-cresol and sulfuric acid (in the molecular proportions of one to two) are warmed together to 35° to melt all *p*-cresol, and the mixture rapidly cooled in an ice-salt mixture, with vigorous stirring, complete solidification occurs *at once*. A white crystalline mass is produced, which melts at 93.5°, and is evidently a pure compound. The reaction is here, so far as can be judged, *instantaneous*, even at the low temperature employed.

This is again in agreement with the theory that the reaction is an oxonium salt formation and ionic in its nature.[3] The basic organic substance, in accordance with its unsaturated nature, is the ionizing medium, and an addition compound (for example, equimolecular) is formed thus:

$$\rangle C{=}O \overset{+}{\underset{-}{}} + H^+ + HSO_4^- \rightleftharpoons \rangle C = O\begin{cases} O(SO_2)OH \\ H \end{cases}.$$

The reaction represented in the above equation is to be regarded either as the first step in the sulfonation process, or as a parallel reaction considerably faster than the one leading to the more stable sulfonic acids.[4] In the former case the completion of the process involves a rearrangement of the molecule and the splitting off of water. Under the latter view, dissociation of the addition compound into the original constituents would take place before sulfonation. The reactions that occur would thus be comparable with those involved in the formation of acetamide by heating ammonium acetate.

The results of the investigation may be summarized in the statement that sulfonation is preceded by the formation of addition compounds,

[1] If sulfonation had taken place a sulfonic acid and water would be present. Sulfonic acids decompose on fusion and have no definite melting points. The only possibility for a constant point of fusion, if we assume sulfonation, is that the sulfonic acid forms a very stable hydrate.

[2] Cohen, *Practical Org. Chem.*, **1904**, p. 150.

[3] Kendall, *J. Am. Chem. Soc.*, **36**, 1242 (1914).

[4] For the suggestion of this second view we are indebted to Professor Stieglitz.

of the nature of oxonium salts. This reaction is *ionic* and *instantaneous*. The addition compounds obtained are possibly—but not necessarily—real intermediate products in the formation of sulfonic acids.

It will be obvious that similar reactions, such as nitration, may be considered to follow an exactly similar course.

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